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$$dF = dU - TdS - SdT$$

$$dF = \overbrace{TdS - pdV}^{\downarrow} - \cancel{TdS} - SdT$$

$$\text{Thus } p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$Z = V \cdot \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$\ln Z = \ln V + \frac{3}{2} \ln\left(\frac{2\pi mkT}{h^2}\right)$$

Thus

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = NkT \frac{\partial}{\partial V}(\ln V)$$

$$p = \frac{NkT}{V} \quad \text{or} \quad pV = NkT.$$

This is ideal gas law.

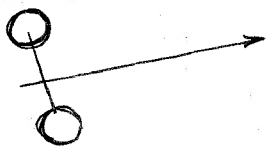
Derived using $\beta = -1/kT$

$$S = k \ln \Omega$$

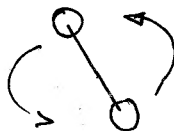
Diatomic Cases.

Monatomic gas - only translational kinetic energy considered.

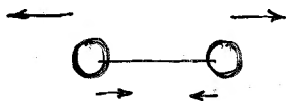
Diatomic molecules - can possess energy by.



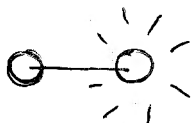
translation



rotation



vibration



electronic
excitation

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Aim - study how different types of energy shape C_v vs T variation.

Simplifying Assumption - can split

total energy ϵ into

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{electronic}}$$

- assumes that rotational state does not affect vibrational etc.
- good approx - not perfect.

(13) Then partition function Z is

$$\begin{aligned} Z &= \sum g \exp\left(-\frac{1}{kT} (\epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e)\right) \\ &= \sum g_t \exp\left(-\frac{\epsilon_t}{kT}\right) \cdot \sum g_r \exp\left(-\frac{\epsilon_r}{kT}\right) \\ &\quad \times \sum g_v \exp\left(-\frac{\epsilon_v}{kT}\right) \cdot \sum g_e \exp\left(-\frac{\epsilon_e}{kT}\right) \end{aligned}$$

i.e. $Z = Z_{\text{trans}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}} \cdot Z_{\text{electronic}}$

$$\ln Z = \ln Z_t + \ln Z_r + \ln Z_v + \ln Z_e$$

Recall

$$C_v = \left(\frac{dU}{dT}\right)_v = \frac{d}{dT} \cdot \left(NkT^2 \frac{d \ln Z}{dT}\right)$$

Thus $C_v = C_v(t) + C_v(r) + C_v(v) + C_v(e)$

Total C_v = sum of contributions of
different motions

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Treat contributions Separately.

1) Translational.

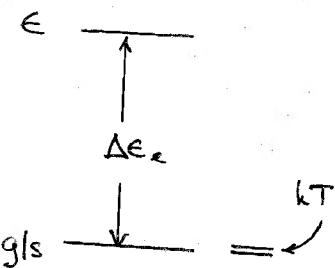
Treated as for monatomic gas.

Translational level spacing $\Delta E \ll kT$

Classical approx valid down to
boiling point of gas.

Get $C_v(t) = \frac{3}{2} Nk.$

2) Electronic excitation of one atom.



Now $\Delta E_e \sim 10 \text{ eV}$

At room temp $kT \sim 0.025 \text{ eV}$

thus $kT \ll \Delta E_e$

$$Z(e) = \exp(-0/kT) + \exp(-\frac{E}{kT})$$

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$$Z(e) = 1 + 0 \dots$$

$$\ln Z = 0$$

$$C_v = 0 \quad - \text{extreme quantum limit.}$$

3/ Vibrational motion

Vibⁿ levels

$$\text{————— } 2h\nu$$

Vibrational

freq ν given by

$$\text{————— } h\nu$$

$$\nu \sim \left(\frac{k}{\mu} \right)^{1/2}$$

$$\text{g/s} \quad \text{————— } 0$$

where k = bond constant

μ = reduced mass of atoms.

$$\text{Energy quantum of vib}^n = h\nu$$

Equivalent temp Θ defined by

$$k\Theta = h\nu$$

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 θ values.

Gas.	θ
O_2	2000 K
N_2	3000 K
H_2	6000 K

At room temp ($T = 300$ K)

$$T \ll \theta$$

Hence $C_v \rightarrow 0$

At higher temps $T \rightarrow 1000$ K - begin to get contribution $C_v(v)$

Then given by vibrator eqn.

$$C_{v(v)} = \frac{Nk \left(\frac{\theta}{T} \right)^2 \exp\left(\frac{\theta}{T} \right)}{\left[\exp\left(\frac{\theta}{T} \right) - 1 \right]^2}$$

For most gases - at temp T where $C_{v(v)}$ begins to contribute - gas molecules dissociate

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4) Rotation. — Levels

9	l		ϵ_r (in $\frac{\hbar^2}{2I}$)
7	3	—————	12

 $l = \text{rot ang mtm.}$

5	2	—————	6
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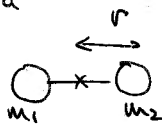
3	1	—————	2
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1	0	—————	0
---	---	-------	---

Rotl levels given by $\epsilon_r = \frac{\hbar^2}{2I} l(l+1)$

where $I = \text{moment of inertia}$

$$= \mu r^2$$



where $\mu = \text{reduced mass} = \frac{m_1 m_2}{(m_1 + m_2)}$

Degeneracy $g = (2l+1)$

Partition fⁿ Z given as

$$Z = \sum g \exp\left(-\frac{\epsilon_r}{kT}\right) = \sum (2l+1) \exp\left(-\frac{\hbar^2 l(l+1)}{2I kT}\right)$$

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Characteristic temperature Φ from

$$k \Phi = \frac{h^2}{2I}$$

Gas.

Φ

O₂

2.1 K

N₂

2.9 K

H₂

85 K

HD

64 K

Gases - except for hydrogen - liquified
at Φ

At $T = 300 \text{ K}$

$T \gg \Phi$

- classical limit.

Can write $Z = \int_0^{\infty} (2l+1) \exp\left(-l(l+1) \frac{\Phi}{T}\right) dl$

Putting $y = l(l+1)$

$$dy = (2l+1) dl$$

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$$Z = \int_0^{\infty} \exp\left(-\frac{y\Phi}{T}\right) dy = T/\Phi$$

$$C_v = \frac{d}{dT} \left(NkT^2 \frac{d}{dT} \ln(T/\Phi) \right)$$
$$= Nk.$$

Classical limit value for rotation.

Sum of contributions for C_v vs T

- see sheet.

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Strange case of H_2 .

For H_2 $\Phi = 85 K$

H_2 - boiling point = 20K - as T

increased from 20K should see growing

contribution from $C_v(r)$

Standard theory

$$Z(r) = \sum_l (2l+1) \exp\left(-\frac{l(l+1)\hbar^2}{2IkT}\right)$$

$$\text{and } C_v(r) = \frac{d}{dT} \left(NkT^2 \frac{d}{dT} \ln Z(r) \right)$$

- gives curve A - see sheet.

This exactly observed for $H D$ where

D = deuterium atom and $\Phi = 64 K$.

For H_2 - expt sees curve C -

how is this explained?

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Difference between HD and H_2 In H_2 - identical particles (fermions)

- must have antisymm w/f.

 H_2 wavefunction written

$$\Psi(H_2) = \Psi(r) \chi(s)$$

↙
rot^e space
w/f

↘ Spin w/f of coupled
protons.

Antisymm total w/f

either $\Psi_p(H_2) = \Psi_s(r) \chi(s=0) \quad l = \text{even}$

or $\Psi_o(H_2) = \Psi_A(r) \chi(s=1) \quad l = \text{odd.}$

where $\chi(s=0) = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow)$

and $\chi(s=1) = \begin{cases} \uparrow\uparrow & M_s = 1 \\ \frac{1}{\sqrt{2}} (\uparrow\downarrow + \downarrow\uparrow) & M_s = 0 \\ \downarrow\downarrow & M_s = -1 \end{cases}$

Q2

$\Psi_P(H_2)$ with $l = \text{even}$ called para

$\Psi_O(H_2)$ with $l = \text{odd}$ called ortho.

Now partition f^n given by

$$Z(\text{rot}^n) = 3 \sum_{l=\text{odd}} (2l+1) \exp\left(-\frac{l(l+1)\hbar^2}{2IkT}\right) + 1 \sum_{l=\text{even}} (2l+1) e^{-\frac{l^2\hbar^2}{2IkT}}$$

Spin degeneracy.

Compute C_v with this Z .

Get curve B on sheet.

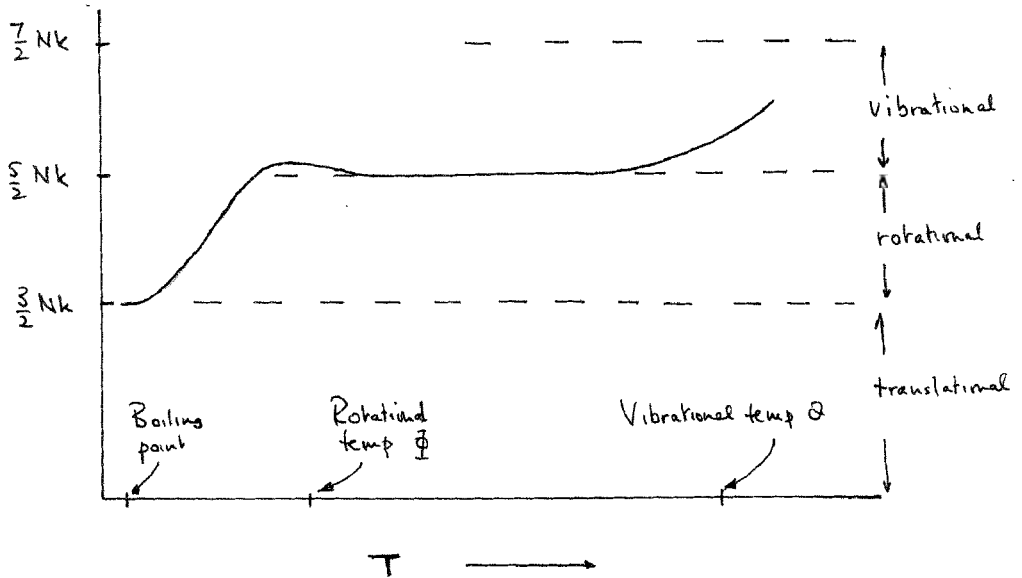
Q. Why does this theory not give expt curve C?

A. If expt done very slowly (or with catalyst) — curve B seen.

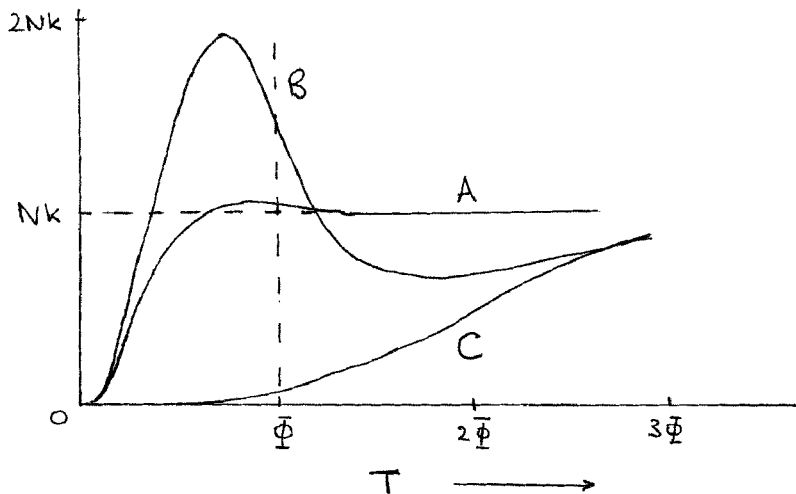
Theory above assumes equilibrium between para and ortho hydrogen.

C_v versus T

Diatomic gases



Rotational C_v for H_2



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In normal conditions - not true.

Energy transferred by collisions -
can change l values.

But ortho \rightleftharpoons para needs change

$$S = 1 \rightleftharpoons S = 0$$

cannot occur in ordinary collision.

Thus ratio $\frac{\text{ortho}}{\text{para}}$ ^{kept} at formation ^{kept} value.

Formation at room temp.

Gives ratio $\frac{\text{ortho}}{\text{para}} = \frac{3}{1}$ (Spin states)

With this ratio unchanged get

$$C_v = \frac{3}{4} C_v(\text{ortho}) + \frac{1}{4} C_v(\text{para}).$$

- this gives curve C .

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General point.

Change in C_v (and other thermodynamic quantities) occurs when

$$kT \sim \epsilon$$

where ϵ is characteristic energy
spacing of particular mechanism.

Inversely.

C_v versus T experiments are valuable
as each feature in graph tells of
a set of energy levels associated
with new mechanism

Quantum gases.

Gas — N particles in a macroscopic
 enclosure — block of metal
 — neutron star..

Recall.

Classical limit

Probability of state occupation $f_i \ll 1$

where $f_i = \frac{n_i}{g_i} = A \exp(-\epsilon_i/kT)$

corresponds to $A \ll 1$.

Quantum limit $A \gg 1$.

Recall $A = \frac{N}{V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2}$

As $T \rightarrow 0$ $A \rightarrow \infty$

(87)

Quantum nature of wavef^{ns} for indistinguishable particles.

- Either
- antisymmetric under particle exchange
 - fermions
 - spin $\frac{1}{2}$, $\frac{3}{2}$...
 - obey Pauli Principle.

- Or
- symmetric under exchange
 - bosons
 - spin 0, 1, ...
 - no Pauli principle

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Fermi Dirac gas.

N weakly interacting fermions.

In conditions where

$A \ll 1$ — can use M. Boltzmann statistics

$A \gg 1$ — use Fermi Dirac statistics.

Procedure

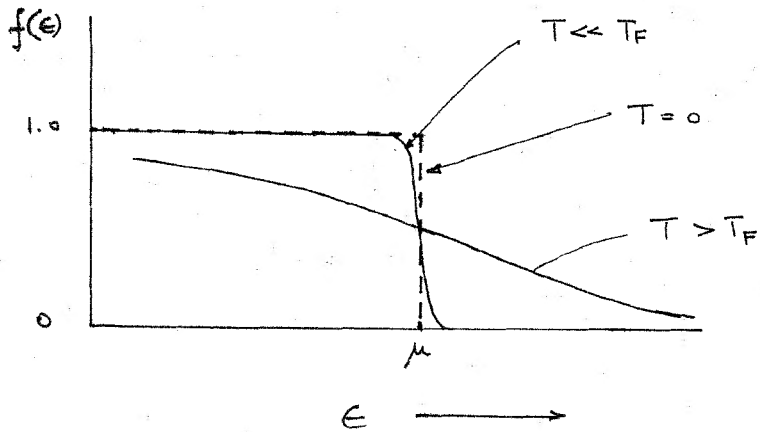
Deduce thermodynamic quantities

$U, C_v, P \dots$ for F-D gas.

Compare predictions to systems

- (1) Conduction electrons in metal
- (2) He^3 atoms in gas and liquid
- (3) Neutrons in white dwarf stars.

Fermi Dirac distribution



Distributions drawn for temperatures

$$T = 0$$

$$T \ll T_F$$

$$T > T_F$$

where Fermi temperature defined as

$$k T_F = \mu$$

μ = Fermi energy.

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Fermi Dirac distribution

Deduced above that probability of state at energy ϵ being occupied was $f(\epsilon)$ where

$$f(\epsilon) = \frac{1}{B \exp(\epsilon/kT) + 1} = \frac{1}{\exp(\frac{\epsilon - \mu}{kT}) + 1}$$

where $B = \exp(-\mu/kT)$

Shape of $f(\epsilon)$ vs ϵ graph - see sheet

Points.

1. In denominator the $+1$ ensures $f < 1$ - obeying Pauli principle
2. For given plot T is constant

(30)

3. Fermi energy μ defined

(i) at $T=0$ $\epsilon = \mu$ is boundary
between filled and empty states

(ii) for $T > 0$ $\epsilon = \mu$ when $f = 1/2$

4. Fermi temperature T_F defined from

$$T_F = \mu / k$$

5. For $0 < T < T_F$ - corners of $T=0$
plot rounded in range kT of

$$\epsilon = \mu$$

For $T \gg T_F$ - graph goes towards
Maxwell Boltzmann shape